## **Supplementary Information**

## Assembly of Polyethyleneimine in the Hexagonal Mesophase of Non-Ionic surfactant: Effect of pH and Temperature

Kamendra P. Sharma<sup>1</sup>, Chandan Kumar Choudhury<sup>2</sup>, Sonal Srivastava<sup>3</sup>, H. Davis<sup>4</sup>, P. R. Rajamohanan<sup>4</sup>, Sudip Roy<sup>2</sup> and Guruswamy Kumaraswamy<sup>11</sup>

<sup>1</sup> Complex Fluids and Polymer Engineering Group, Polymer Science and Engineering Division, National Chemical Laboratory, Pune, India.

<sup>2</sup> Physical Chemistry Division, National Chemical Laboratory, Pune, India.

<sup>3</sup> Chemical Engineering Department, IIT Kharagpur, India.

<sup>4</sup> NMR Center, National Chemical Laboratory, Pune, India.

g.kumaraswamy@ncl.res.in

<sup>&</sup>lt;sup>1</sup> Correspondence to: Guruswamy Kumaraswamy, Complex Fluids and Polymer Engineering

Group, Polymers and Advanced Materials Building, National Chemical Laboratory, Dr. Homi

Bhabha Road, Pune 411008, India. Tel: 91-20-2590-2182; Fax: 91-20-2590-2618; Email:



Figure S0 a: TLC plates of the surfactant,  $C_{12}E_9$  used in the experiments reported here (transition temperature,  $T_{HI}$  for 50/50 surfactant/water is 50°C). The plates were stained with tincture iodine after being immersed in (a) 10:90 and (b) 15:85 (% by volume) of petroleum ether and ethyl acetate mixture respectively. We observe multiple spots qualitatively indicating the presence of numerous components in the surfactant. We observe that, for surfactant from a different bottle (for which the transition temperature,  $T_{HI}$  for 50/50 surfactant/water is 44°C) TLC using a solvent containing 15:85 (% by volume) of petroleum ether and ethyl acetate mixture respectively, separates into a different number of spots (Figure S0 c). This indicates that the bottle to bottle variation in the surfactant composition is correlated with the change in the observed  $T_{HI}$ . Both bottles of surfactant were obtained from Sigma Aldrich, and the surfactant was used without any further treatment.



Figure S0 b: HPLC of the  $C_{12}E_9$  surfactant on a Waters HPLC. The mobile phase used was methanol and detection was using an RI detector, since the surfactant did not absorb in the UV-Vis region. The column used for resolution was a C8-Zorbax column.



Figure S1: Specific Viscosity vs concentration for 2000 g.mol<sup>-1</sup> PEI at different pH values by using (a) HNO<sub>3</sub>, and (b) HCl.



Figure S2. SAXS spectra for neat H<sub>1</sub> phase at (a) pH 12.8, (b) pH 5 and (c) pH 1. The transition temperature,  $T_{HI}$  of the H<sub>1</sub> phase at three different pH values is ~50-51°C.



Figure S3. Snapshots of sample of 5 wt% PEI in 47.5%/47.5% (by weight) of  $C_{12}E_9/H_2O$  at pH 5 from (a ) 25°C and (b) at 17°C.



Figure S4. Snapshot of sample of 5% PEI in 47.5%/47.5% (by weight)  $C_{12}E_9/H_2O$  at 25°C at pH 1.



Figure S5. Optical micrographs under parallel polarizers for all the samples at 45°C. The black spots are impurities on the lens (these do not move as the sample is moved)



Figure S6. Optical micrograph of polymer rich droplets formed at room temperature i.e.  $\sim 28^{\circ}$ C in a 5 wt% PEI in 47.5%/47.5% (by weight) C<sub>12</sub>E<sub>9</sub>/H<sub>2</sub>O system at pH 1. Scale bar refers to 50 µm.



Figure S7. Complete 2-D ROESY spectrum for 5% PEI in 25 wt% C<sub>12</sub>E<sub>9</sub> in D<sub>2</sub>O at (a) pH 12.8, (b) pH 5 and (c) pH 1.



Figure S8. Pair distribution plots for 20-mer PEI in water (a) Nearest Neighbour (NN) ; and (b) Next -Nearest Neighbour (NNN) Distribution.



Figure S9: Measured <sup>1</sup>H NMR spectra for PEI in  $H_2O$  (top) and in  $H_2O/D_2O$  mixture (bottom), prepared as mentioned in the main manuscript.

We do not measure pD in our experiments. We report pH\*, viz. we use an electrode that is calibrated for measuring pH in H<sub>2</sub>O, and use it to make measurements in the D<sub>2</sub>O/H<sub>2</sub>O mixtures in our samples. Recently, Krezel and Bal (Krezel, A; Bal, W. J. Inorg. Biochem. **2004**, *98*, 161) have reported that there is a linear relation between the pH\* and pH:

$$pH = 0.929 pH^* + 0.42$$

However, we cannot directly use this relationship to calculate the  $[D^+]$  in our experiments since (a) we are unable to eliminate H<sub>2</sub>O and use H<sub>2</sub>O/D<sub>2</sub>O mixtures to prepare our NMR samples, and (b) we use HNO<sub>3</sub> to acidify our samples. Thus, the protonated species formed in our experiments can be either HD<sub>2</sub>O<sup>+</sup> or H<sub>3</sub>O<sup>+</sup>. However, if we still use the aforementioned expression to calculate the pH, we obtain pH = 1.349; 5.065 and 12.31 for the reported pH\* = 1, 5 and 12.8. To evaluate the influence of the difference between the measured and actual value of pH on our experiments, we have conducted <sup>1</sup>H NMR measurements on our sample in H<sub>2</sub>O and in H<sub>2</sub>O/D<sub>2</sub>O, under identical conditions of measured pH (viz. pH for the sample in H<sub>2</sub>O and pH\* for the sample in H<sub>2</sub>O/D<sub>2</sub>O). The NMR patterns obtained are very similar, even though they are not qualitatively identical. As expected, there are differences are minor. Therefore, we anticipate that there is no qualitative consequence to the conclusions that we arrive at.



Figure S10: Pair distribution between the carbon atoms present in the PEI chain and the carbon atoms in the hydrophobic part of the surfactant molecules.

Polyethyleneimine (PEI)			
	No pro	otonation	Protonated
N Terminal			
Terminal N	-0.740		-0.417
H attached to N	0.250		0.360
C next to N, CA	-0.140		0.056
H attached to CA, HA	0.115		0.087
C attached to CA, CB	-0.080		-0.147
H attached to CB, HB	0.115		0.127
Repeating Unit			
Ν	-0.593		-0.150
H connected to N	0.269		0.340
C next to N, CA	-0.086		-0.23
H attached to CA, HA	0.124		0.129
C attached to CA, CB	-0.086		-0.023
H attached to CB, HB	0	.124	0.129
C Terminal			
Ν	-0.500		-0.135
H connected to N	0.280		0.331
C next to N, CA	-0.081		0.067
H attached to CA, HA	0.125		0.120
C attached to CA, CB	-0.300		-0.314
H attached to CB, HB	0.117		0.160
Surfactant (Nonaethylene glycol monododecyl ether, C <sub>12</sub> E <sub>9</sub> )			
C-Terminal			
C		-0.180	
Repeating CH <sub>2</sub> units [not adjacent to O]			
C		-0.120	
H 0.060			0.060
All CH <sub>2</sub> units adjacent to O			
		0.140	
H		0.030	
All non-terminal O			
<u> </u>			
Terminal O			
0		-0.683	
Н		0.423	

Table S1. The summary of charges and atom types used for the simulation of all the components in the system.